

CLAY AND ASSOCIATED MINERALS IN BATTERY INDUSTRY

14.1 MANGANESE MINERAL

Manganese is found in combination with iron and in many minerals in nature. Some manganese minerals are pyrolusite (MnO_2), braunite ($3\text{Mn}_2\text{O}_3 \cdot \text{MnSiO}_3$), rhodochrosite (MnCO_3), rhodonite (MnSiO_3), manganite ($\text{Mn}_2\text{O}_3 \cdot \text{H}_2\text{O}$) etc. Manganese ore is produced in huge quantity in India. The total reservoir of manganese ore deposits in India as per IBM report, are placed at ground 154 million tonnes (with proved 18 million tonnes and probably 38 million tonnes and possible 98 million tonnes).

World War II-era nickel made from a 56% copper, 35% silver, 9% manganese alloy. Methyl cyclopentadienyl manganese tricarbonyl is used as an additive in unleaded gasoline to boost octane rating and reduce engine knocking. Manganese oxide (manganese dioxide, MnO_2) is used as a reagent in organic chemistry for the oxidation of benzylic alcohols (i.e. adjacent to an aromatic ring). MnO_2 is also used in the manufacture of oxygen and chlorine, and in drying black paints. In some preparations, it is a brown pigment that can be used to make paint. The metal is very occasionally used in coins; until 2000, the only United States coin to use manganese was the “wartime” nickel during 1942-1945. An alloy of 75% copper and 25% nickel was traditionally used for the production of nickel coins. However, because of shortage of nickel metal during the war, it was substituted by more available silver and manganese, thus resulting in an alloy of 56% copper, 35% silver and 9% manganese. Manganese compounds have been used as pigments and for the colouring of ceramics and glass. In the glass industry, manganese compounds are also used. Manganese reacts with iron to induce a strong green colour in glass by forming

less-coloured iron and slightly pink manganese, compensating for the residual colour of the iron. Larger amounts of manganese are used to produce pink coloured glass.

Manganese ore is also used in the making of batteries which have 80-86 per cent of manganese oxide, while the content of iron and aluminium should not exceed 10 per cent. Chemistry of primary and rechargeable battery is given in Tables 14.2 and 14.3. Nowadays, of course, low-grade manganese ores are used after purification in the making of batteries.

Table 14.1: Mineral constituents of battery

<i>Mineral constituents</i>	<i>Battery grade (per cent)</i>
MnO ₂	80-84
Total iron-content (including magnetic iron)	Less than 2.5
Fe ₂ O ₃ +Al ₂ O ₃	Max. 10
Cu	Less than 0.3
Acid soluble	Max. 10

Manganese mineral deposits are observed mainly as five types from aspect of origin. These are hydrothermal deposit, sedimentary deposit, residual deposit, metasomatic replacement deposit and metamorphic deposit. Manganese ore is principally used in the manufacture of ferro-manganese and steel. Moreover, it is also used in small quantities in paint and glass. In dry cell batteries *manganese dioxide* is used. Manganese ore is basically mined in Madhya Pradesh, Andhra Pradesh, Orissa, Maharashtra and Karnataka. Though the manganese ore occurred at different places in Indian Plateau, it is found in large quantities in Bhandara, Nagpur and Balaghat districts. These places are situated close to each other in the central and western regions of the country. Of the total manganese ore reserves in the country, Balaghat-Nagpur-Bhandara manganese belt accounts for a huge portion. Orissa is considered as the leading producer of manganese ore in the country. In these states, manganese ore is mainly mined in Keonjhar and Sundargarh districts. These two districts are leading manganese ore producers with huge tonnes of production. After Orissa, Karnataka is second leading producer of manganese ore in the country. Here, manganese ore is mainly mined in Bellary, Shimoga and North Kanara districts. Further, Nagpur and Bhandara districts of Maharashtra, and Balaghat district of Madhya Pradesh are other important places where manganese ore is mined. Manganese minerals are also produced as manganese nodules lie on the seabed sediment, often partly or completely buried. They vary greatly in abundance, in some cases touching one another and covering more than 70% of the sea floor.



Fig. 14.1: Manganese minerals.

14.2 DEVELOPMENT OF BATTERIES

Battery is a collection of multiple electrochemical cells, but in popular usage battery often refers to a single cell. It converts stored chemical energy into electrical energy. The first electrochemical cell was developed by the Italian physicist Alessandro Volta in 1792, and in 1800 he invented the first battery, a “pile” of many cells in series. Although early batteries were of great value for experimental purposes, in practice their voltages fluctuated and they could not provide a large current for a sustained period. Later, starting with the Daniell cell in 1836, batteries provided more reliable currents and were adopted by industry for use in stationary devices. These wet cells used liquid electrolytes, which were prone to leakage and spillage if not handled correctly. Many used glass jars to hold their components, which made them fragile. These characteristics made wet cells unsuitable for portable appliances. Near the end of the nineteenth century, the invention of dry cell batteries, which replaced the liquid electrolyte with a paste, made portable electrical devices practical. Since then, batteries have gained popularity as they became portable and useful for a variety of purposes.

14.3 TWO TYPES OF BATTERIES

Primary Batteries

These batteries irreversibly transform chemical energy to electrical energy. When the initial supply of reactants is exhausted, energy cannot be readily restored to the battery by electrical means, so these batteries are designed to be used once and discarded. Thus these are also called disposable batteries. Common types of disposable batteries include zinc-carbon batteries and alkaline batteries. In general, these have higher energy densities than rechargeable batteries.

Secondary Batteries

These batteries are designed to be recharged and used multiple times. That is, they can have their chemical reactions reversed by supplying electrical energy to the cell, restoring their original composition. Thus these are also called rechargeable batteries. Cells of this type include nickel-cadmium (NiCd), nickel-zinc (NiZn), and lithium-ion (Li-ion) cells.

14.4 PRINCIPLE OF OPERATION

A battery is a device that converts chemical energy directly to electrical energy. It consists of a number of voltaic cells; each voltaic cell consists of two half-cells connected in series by a conductive electrolyte containing anions and cations. One half-cell is anode and another is cathode. In the redox reaction, cations are reduced (electrons are added) at the cathode, while anions are oxidized (electrons are removed) at the anode. The electrodes do not touch each other but are electrically connected by the electrolyte. Each half-cell has an electromotive force (or emf), determined by its ability to drive electric current from the interior to the exterior of the cell. The net emf of the cell is the difference between the emfs of its half-cells, as first recognized by Volta. The electrical driving force of a cell is known as the terminal voltage, measured in volts. The terminal voltage of a cell that is neither charging nor discharging is called the open-circuit voltage. An ideal cell has negligible internal resistance, so it would maintain a constant terminal voltage until exhausted, then dropping to zero. If such a cell maintained 1.5 volts and stored a charge of one coulomb then on complete discharge it would perform 1.5 joule of work. So, the voltage developed depends on the energy release of the chemical reactions of its electrodes and electrolyte.

14.5 BATTERY CELL TYPES

There are many general types of electrochemical cells, the variation includes galvanic cells, electrolytic cells, fuel cells and flow cells.

Wet Cell

A wet cell battery has a liquid electrolyte. It is also called as flooded cell, since the liquid covers all internal parts. Wet cells were a precursor to dry cells and are commonly used as a tool for electrochemistry. A particular type of wet cell known as a concentration cell is important in understanding corrosion. Wet cells may be primary or secondary cells. Some other primary wet cells are the Leclanche cell, Grove cell, Bunsen cell, chromic acid cell, etc. Wet cells are used in automobile batteries and telecommunication.

Dry Cell

A dry cell has the electrolyte immobilized as a paste, with only enough moisture

in the paste to allow current to flow. As opposed to a wet cell, the battery can be operated in any random position, and will not spill its electrolyte if inverted.

While a dry cell's electrolyte is not truly completely free of moisture and must contain some moisture to function, it has the advantage of containing no sloshing liquid and consequently making it highly suitable for small portable electric devices.

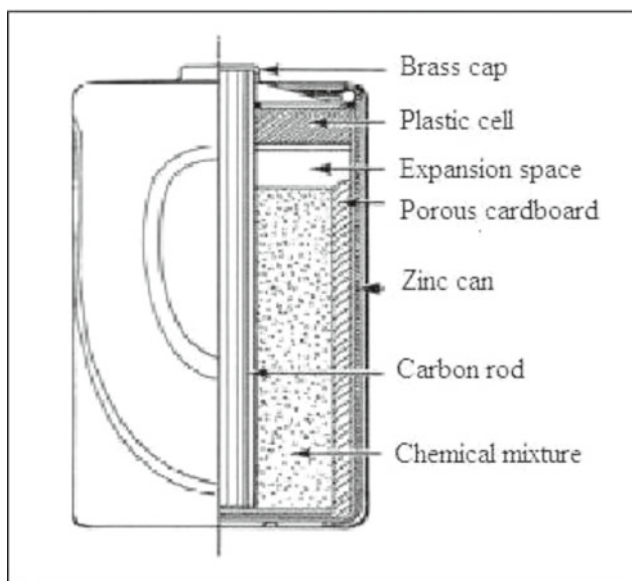


Fig. 14.2: Schematic diagram of a dry cell.

A common dry cell battery is the zinc-carbon battery, using dry Leclanché cell, with a nominal voltage of 1.5 volts.

A standard dry cell is made with a zinc anode (negative pole), in the form of a cylindrical pot, with a carbon cathode (positive pole) in the form of a central rod. The electrolyte is ammonium chloride in the form of a paste. Ammonium chloride and manganese dioxide are present in the remaining space between the electrolyte and carbon cathode. In some modern types of 'high-power' batteries, the ammonium chloride has been replaced by zinc chloride.

14.6 MOLTEN SALT BATTERY

A molten salt battery is a primary or secondary battery that uses a molten salt as its electrolyte. Molten salt batteries are a class of primary cell and secondary cell high-temperature electric battery. These types of batteries are used where high energy density and high power density are required. Their energy density and power density give them potential for use in electric vehicles.

14.7 RESERVE BATTERY

A reserve battery can be stored for a long period of time and is activated when its internal parts are assembled. For example, a battery for an electronic fuse might be activated by the impact of firing a gun, breaking a capsule of electrolyte to activate the battery and power the fuse's circuits. In this condition, chemical deterioration or self-discharge is essentially eliminated, and the battery is capable of long-term storage. Usually the electrolyte is the component that is isolated. The reserve battery design is used to meet extremely long or environmentally severe storage requirements that cannot be met with an "active" battery designed for the same performance characteristics. These batteries are used, for example, to deliver high power for relatively short periods of time, in missiles and other weapon systems.

14.8 FASTEST CHARGING AND LARGEST BATTERIES

Lithium iron phosphate (LiFePO_4) batteries were the fastest-charging and discharging batteries (supercapacitors, in some ways comparable to batteries, charge faster). The world's largest battery, composed of Ni-Cd cells, is in Fairbanks, Alaska. Sodium-sulphur batteries were being used to store wind power. Lithium-sulphur batteries have been used on the longest and highest solar-powered flight. The speed of recharging of lithium-ion batteries can be increased by manufacturing changes.

14.9 BATTERY CAPACITY AND DISCHARGING

A battery's cell performance may vary over load cycle, over charge cycle, and over lifetime due to many factors including internal chemistry and temperature.

A battery's *capacity* is the amount of electric charge which the battery can store. If there is more electrolyte and electrode material in the cell, capacity of the cell will be greater. A small cell has less capacity than a larger cell with the same chemistry. Because of the chemical reactions within the cells, the capacity of a battery depends on the discharge conditions such as the magnitude of the current. If a battery is discharged at a relatively high rate, the available capacity will be lower than expected.

The relationship between current, discharge time, and capacity for a lead acid battery is approximated (over a certain range of current values) by Peukert's law:

$$t = \frac{Q_p}{I^k}$$

where Q_p is the capacity when discharged at a rate of 1 amp., I is the current drawn from battery, t is the amount of time (in hours) that a battery can sustain and k is a constant around 1.3.

In practical batteries, internal energy losses and limited rate of diffusion of ions through the electrolyte cause the efficiency of a battery to vary at different discharge rates. When discharging at low rate, the battery's energy is delivered more efficiently than at higher discharge rates, but if the rate is too low, it will self-discharge during the long time of operation, again lowering its efficiency.

14.10 BATTERY CHEMISTRY

A battery is a package of one or more galvanic cells used for the production and storage of electric energy by chemical means. A galvanic cell consists of at least two half cells, a reduction cell and an oxidation cell. Chemical reactions in the two half cells provide the energy for the galvanic cell operations. Each half cell consists of an electrode and an electrolyte solution. Usually the solution contains ions derived from the electrode by oxidation or reduction reaction. It can be demonstrated through a galvanic cell which is also called a voltaic cell. The spontaneous reactions in it provide the electric energy or current. Two half cells can be put together to form an electrolytic cell, which is used for electrolysis. In this case, electric energy is used to force non-spontaneous chemical reactions. Oxidation and reduction both play an important role. Oxidation indicates loss of electrons and gain of electrons indicated by reduction. Oxidation and reduction reactions cannot be carried out separately. They have to appear together in a chemical reaction. Thus oxidation and reduction reactions are often called redox reactions. In terms of redox reactions, a reducing agent and an oxidizing agent form a redox. An oxidant is an oxidizing reagent, and a reductant is a reducing agent.

Table 14.2: Chemistry of primary battery

<i>Chemistry</i>	<i>Cell voltage</i>	<i>Specific energy [MJ/kg]</i>	<i>Comments</i>
Zinc-carbon	1.5	0.13	Inexpensive
Zinc-chloride	1.5		Inexpensive
Lithium (lithium-manganese dioxide) LiMnO ₂	3.0	0.83-1.01	Expensive only used in high-drain devices
Nickel oxyhydroxide	1.7		Good for high drain uses
Silver-oxide	1.55	0.47	Very expensive only used commercially in 'button' cells
Zinc-air	1.35-1.65	1.59	Mostly used in hearing aids
Alkaline	1.5	0.4-0.59	Good for high and low drain uses

Table 14.3: Chemistry of rechargeable battery

<i>Chemistry</i>	<i>Cell voltage</i>	<i>Specific energy [MJ/kg]</i>	<i>Comments</i>
NiCd	1.2	0.14	Inexpensive, used in higher drain devices
Lead-acid	2.1	0.14	Moderately expensive, used in automobile batteries
NiMH	1.2	0.36	Moderately inexpensive, used in some cars
Lithium ion	3.6	0.46	Very expensive, used in laptop computers, moderate to high-end digital cameras and camcorders, and cellphones

14.11 HOME-MADE CELLS

Almost any moist object that has enough ions to be electrically conductive can serve as the electrolyte for a cell. It is possible to insert two electrodes made of different metals into a lemon, potato, etc. and generate small amounts of electricity. Home-made cells of this kind are of no real practical use, because they produce far less current—and cost far more per unit of energy generated—than commercial cells.

Lead acid cells can easily be manufactured at home, but a tedious charge/discharge cycle is needed to ‘form’ the plates. This is a process in which lead sulfate forms on the plates, and during charge is converted to lead dioxide (positive plate) and pure lead (negative plate). Repeating this process increases the current that cell can deliver.

- ➔ Aluminium-air batteries can also be produced with high-purity aluminium.
- ➔ Aluminium foil batteries will produce some electricity, but they are not very efficient, in part because a significant amount of hydrogen gas is produced.

14.12 HAZARDS

Explosion

A battery explosion is caused by the malfunction of a battery, such as attempting to recharge a primary (non-rechargeable) battery. Explosions are most likely to occur in car batteries when a short circuit generates very large currents. In addition, car batteries liberate hydrogen when they are overcharged because of electrolysis of the water in the electrolyte. When a battery is recharged at an excessive rate, an explosive gas mixture of hydrogen and oxygen may be

produced faster than it can escape from within the walls of the battery, leading to pressure build-up and the possibility of bursting of the battery case. In extreme cases, the battery acid may spray violently from the casing of the battery and cause injury.

Leakage

Many battery chemicals are corrosive, poisonous, or both. If leakage occurs, either spontaneously or through accident, the chemicals released may be dangerous.



Fig. 14.3: Leaked alkaline battery.

14.13 BATTERY LIFETIME

Primary batteries

Even if never taken out of the original package, primary batteries can lose 8 to 20 per cent of their original charge every year at a temperature of about 20°–30°C. This is known as the “self discharge” rate and is due to side chemical reactions, which occur within the cell even if no load is applied to it. The rate of the side reactions is reduced if the batteries are stored at low temperature, although some batteries can be damaged by freezing because high or low temperatures may reduce battery performance.

Secondary batteries

Storage life of secondary batteries is limited by chemical reactions (side reactions) that occur between the battery parts and the electrolyte. Due to this reaction internal parts may corrode and fail, or the active materials may be slowly converted to inactive forms and may be lost due to physical changes of volume; this may limit the life of the battery.

In old chemistry rechargeable batteries self-discharge more rapidly occurred than disposable alkaline batteries, especially nickel-based batteries. However,



Fig. 14.4: Photograph of a dry cell battery.

newer low self-discharge nickel metal hydride (NiMH) batteries designs have reduced the self-discharge rate to a relatively low level. Most nickel-based batteries are partially discharged when purchased, and must be charged before first use. Newer NiMH batteries are ready to be used when purchased, and have only 15% discharge in a year. Rechargeable batteries have their energy content restored by charging. Low-capacity NiMH batteries can be charged for about 1000 cycles, whereas high-capacity NiMH batteries can be charged for about 500 cycles

Automotive lead-acid rechargeable batteries have a much harder life. The main benefit of the lead-acid battery is its low cost; the main drawbacks are its large size and weight for a given capacity and voltage. Lead-acid batteries should never be discharged to below 20% of their full capacity, because internal resistance will cause heat and damage when they are recharged.

Extending Battery Life

Battery life can be extended by storing the batteries at a low temperature, as in a refrigerator or freezer, which slows the chemical reactions in the battery. Such storage can extend the life of alkaline batteries by about 5%, while the charge of rechargeable batteries can be extended from a few days up to several months.

Prolonging Life in Multiple Cells through Cell Balancing

Battery pack cells are balanced when all the cells in the battery pack meet two conditions:

1. If all cells have the same State of Charge (SOC) and same capacity, they are balanced. In this case, the Open Circuit Voltage (OCV) is a good measure

of the SOC. In an out of balance pack, all cells can be differentially charged to full capacity.

2. If the cells have different capacities but same State of Charge (SOC), they are also considered balanced when the SOC is the same. But, since SOC is a relative measure, the absolute amount of capacity for each cell is different. To keep the cells with different capacities at the same SOC, cell balancing must provide differential amounts of current to cells.

14.14 ENVIRONMENTAL CONCERNS

The widespread use of batteries has created many environmental concerns, such as toxic metal pollution. Battery manufacture consumes resources and often involves chemical hazards. Used batteries also contribute to electronic waste. Some areas now have battery recycling services available to recover some of the materials from used batteries. Recycling or proper disposal prevents dangerous elements (such as lead, mercury and cadmium) found in some types of batteries from entering the environment. In the United States, the Mercury Containing and Rechargeable Battery Management Act of 1996 banned the sale of mercury-containing batteries, enacted uniform labeling requirements for rechargeable batteries, and required that rechargeable batteries be easily removable.

QUESTIONS

1. What are the mineral constituents of battery?
2. What is the role of manganese dioxide in formation of battery?
3. Describe the following items with description:
Molten salt battery, Reserve battery, Fastest charging, largest and lightest batteries, Battery capacity and discharging.
4. What is dry cell and wet cell?
5. What is chemistry of primary battery and rechargeable battery?
6. Give an idea about the type of hazards made by battery?

FURTHER READING

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